

California Environmental Protection Agency



METHOD 310

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOC) IN CONSUMER PRODUCTS AND REACTIVE ORGANIC COMPOUNDS IN AEROSOL COATING PRODUCTS

(Including Appendices A and B)

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Amended: ***

DISCLAIMER: Mention of any trade name or commercial product in Method 310 does not constitute endorsement or recommendation of this product by the Air Resources Board.

METHOD 310

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOC) IN CONSUMER PRODUCTS AND REACTIVE ORGANIC COMPOUNDS IN AEROSOL COATING PRODUCTS

1 APPLICABILITY

1.1 This method (Method 310) applies to the determination of the percent by weight of:

(1) volatile organic compounds (VOC) in consumer products, antiperspirant and deodorant products, and aerosol coatings products as those terms are defined in Title 17, California Code of Regulations (CCR), Division 3, Chapter 1, Subchapter 8.5 (Consumer Products), commencing with section 94500, and

(2) low vapor pressure-volatile organic compounds (LVP-VOC) as that term is defined in section 94508(a)(~~78~~ ***), and

(3) the reactive organic compounds (ROC) contained in aerosol coating products, as that term is defined in Title 17, CCR, section 94521.

1.2 Method 310 determines the total volatile material in a product and the presence of any compounds prohibited by ARB regulations ("prohibited compounds"). Components of the product that do not meet the definition of a VOC or are exempted by ARB regulations for a specific product category ("exempt compounds") are subtracted from the total volatile material to determine the final VOC content for the product. Method 310 is also used to determine the percent by weight of the ROCs contained in aerosol coating products, for the purpose of determining compliance with the Regulation for Reducing the Ozone Formed from Aerosol Coating Product Emissions, Title 17, CCR, sections 94520 to 94528 (the "Aerosol Coatings Regulation").

1.3 Method 310 does not apply to the determination of the composition or concentration of fragrance components in products.

1.4 The term "Executive Officer" as used in this document means the Executive Officer of the Air Resources Board or his or her authorized representative.

2 TEST METHODS

Method 310 incorporates by reference the following American Society for Testing and Materials (ASTM), National Institute for Occupational Safety and Health (NIOSH), and United States Environmental Protection Agency (US EPA) analytical test methods:

2.1 ASTM D 2369-~~97~~ 03: Standard Test Method for Volatile Content of Coatings (~~July 10, 1997~~).

- 2.2 ASTM D 1426-~~93~~ 03: Standard Test Methods for Ammonia Nitrogen in Water (~~September 15, 1993~~).
- 2.3 ASTM D 4017-~~96a~~ 02: Standard Test Method for Water in Paints and Paint Materials by the Karl Fisher Titration Method (~~July 10, 1996~~).
- 2.4 ASTM D 3792-~~91~~ 99: Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection Into a Gas Chromatograph (~~May 15, 1991~~).
- 2.5 ASTM D 859-~~94~~ 00: Standard Test Method for Silica in Water (determination of polymethylsiloxanes after digestion) (~~May 15, 1994~~).
- 2.6 ASTM D 3074-94: Standard Test Methods for Pressure in Metal Aerosol Containers (~~November 15, 1994~~) (*withdrawn 2000, no replacement*) with the modifications found in Appendix A to this Method 310.
- 2.7 ASTM D 3063-94: Standard Test Methods for Pressure in Glass Aerosol Bottles (~~November 15, 1994~~) (*withdrawn 2000, no replacement*) with the modifications found in Appendix A to this Method 310.
- 2.8 ASTM D 3064-~~89~~ 97: Standard Terminology Relating to Aerosol Products (~~November 24, 1989~~).
- 2.9 NIOSH: Method 1400 Alcohols I (analysis of acetone and ethanol by gas chromatography). NIOSH Manual of Analytical Methods, Volume 1 (~~February 1984~~ August 1994).
- 2.10 Gas Chromatography/Mass Spectrometry for Volatile Organics (analysis of exempt and prohibited compounds in the product by headspace/gas chromatography/mass spectrometry).
- 2.10.1 US EPA Method 8240B, September 1994, Revision 2, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Test Methods for Evaluating Solid Waste, Volume 1 B, Chapter 4, Section 4.3.2: Laboratory Manual Physical/Chemical Methods, SW-846, September 1994.
- 2.10.2 US EPA Method 8260B, December 1996, Revision 2, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Test Methods for Evaluating Solid Waste, Volume 1 B, Chapter 4, Section 4.3.2: Laboratory Manual Physical/Chemical Methods, SW-846, December 1996.
- 2.11 US EPA Reference Method 24, Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings: 40 Code of Federal Regulations (CFR) Part 60, Appendix A, as it existed on ~~July 1, 1994~~ September 11, 1995.

- 2.12 US EPA Reference Method 24A, Determination of Volatile Matter Content and Density of Printing Inks and Related Coatings: 40 CFR Part 60, Appendix A, as it existed on July 1, 1994.
- 2.13 US EPA Reference Method 18, Measurement of Gaseous Organic Compound Emissions by Gas Chromatography: 40 CFR Part 60, Appendix A, as it existed on ~~July 1, 1994~~ September 25, 1996.
- 2.14 US EPA Method 300.7, March 1986. Dissolved Sodium, Ammonium, Potassium, and Calcium in Wet Deposition by Chemically Suppressed Ion Chromatography.
- 2.15 ASTM D 86-~~96~~ 03: Standard Test Methods for Distillation of Petroleum Products (~~April 10, 1996~~).
- 2.16 ASTM D 850-~~93~~ 03: Standard Test Methods for Distillation of Industrial Aromatic Hydrocarbons and Related Materials (~~April 15, 1993~~).
- 2.17 ASTM D 1078-~~97~~ 03: Standard Test Methods for Distillation Range of Volatile Liquids (~~July 10, 1997~~).
- 2.18 ASTM D 2879-97: Standard Test Method for Vapor-Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope (~~April 10, 1997~~) with the modifications found in Appendix B to this Method 310.
- 2.19 ASTM D 2887-~~97~~ 02: Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography (~~April 10, 1997~~).
- 2.20 ASTM E 1719-97: Standard Test Method for Vapor Pressure of Liquids by Ebulliometry (~~March 10, 1997~~).

3 CONSUMER PRODUCTS TESTING PROCEDURE

- 3.1 The testing begins when the Executive Officer selects a product for analysis by Method 310. The Executive Officer will maintain sample chain of custody throughout the selection and analytical process.

- 3.2 Initial Testing of Aerosol Products

If the sample is an aerosol product, the aerosol propellant is separated from the ~~liquid~~ non-propellant portion of the product by using ASTM D 3074-94 (as modified in Appendix A for metal aerosol container) or ASTM D 3063-94 (as modified in Appendix A for glass aerosol container). The propellant portion is analyzed for exempt or prohibited compounds by using US EPA Reference Method 18. The remaining ~~liquid~~ non-propellant portion of the product is then analyzed as specified in section 3.3.

- 3.3 Initial Testing of Non-Aerosol Products and the ~~Liquid~~ Non-Propellant Portion of Aerosol Products

The ~~liquid, solid, or gel~~ ***non-aerosol or non-propellant portion of an aerosol*** product ~~sample~~ is analyzed to determine the total volatile material present in the sample and to determine the presence of any exempt or prohibited compounds. This analysis is conducted by performing the following tests:¹

- 3.3.1 Gravimetric analysis of samples to determine the weight percent of total volatile material, using US EPA Reference Methods 24/24A, ASTM D 2369-~~97~~ 03.
- 3.3.2 Determination of sample water content. For determination of water content either ASTM D 4017-~~96a~~ 02, or ASTM D 3792-~~91~~ 99 may be used, or results from both procedures may be averaged and that value reported.
- 3.3.3 Determination of ammonium content using ASTM D 1426-~~93~~ 03 or US EPA Method 300.7.
- 3.3.4 Determination of ketones and alcohol content using NIOSH Method 1400.
- 3.3.5 Analysis of exempt and prohibited compounds, if present (US EPA Reference Method 18, US EPA Method 8240B, US EPA Method 8260B, ASTM D 859-~~94~~ 00, NIOSH Method 1400).
- 3.3.6 If LVP-VOC status is claimed or the analysis indicates the presence of an LVP-VOC component and the percent VOC is not in compliance, the Executive Officer will request formulation data as specified in Section 3.5.2.

3.4 Prohibited Compounds

If the sample is found to contain compounds prohibited by ARB regulations (i.e., ozone-depleting compounds) at concentrations equal to or exceeding 0.1 percent by weight, the Executive Officer will reanalyze the sample for confirmation.

3.5 Initial Determination of VOC Content

The Executive Officer will determine the VOC content pursuant to sections 3.2 and 3.3. Only those components with concentrations equal to or greater than 0.1 percent by weight will be reported.

- 3.5.1 Using the appropriate formula specified in section 4.0, the Executive Officer will make an initial determination of whether the product meets the applicable VOC standards specified in ARB regulations. If initial results show that the product does not meet the applicable VOC standards, the Executive Officer may perform additional testing to confirm the initial results.

¹ Alternate test methods may be used, as provided in section 7.0

- 3.5.2 If the results obtained under section 3.5.1 show that the product does not meet the applicable VOC standards, the Executive Officer will request the product manufacturer or responsible party to supply product formulation data. The manufacturer or responsible party shall supply the requested information. Information submitted to the ARB Executive Officer may be claimed as confidential; such information will be handled in accordance with the confidentiality procedures specified in Title 17, California Code of Regulations, sections 91000 to 91022.
- 3.5.3 If the information supplied by the manufacturer or responsible party shows that the product does not meet the applicable VOC standards, then the Executive Officer will take appropriate enforcement action.
- 3.5.4 If the manufacturer or responsible party fails to provide formulation data as specified in section 3.5.2, the initial determination of VOC content under this section 3.5 shall determine if the product is in compliance with the applicable VOC standards. This determination may be used to establish a violation of ARB regulations.
- 3.6 Determination of the LVP-VOC status of compounds and mixtures. This section does not apply to antiperspirants and deodorants or aerosol coatings products because there is no LVP-VOC exemption for these products.
- 3.6.1 Formulation data. If the vapor pressure is unknown, the following ASTM methods may be used to determine the LVP-VOC status of compounds and mixtures: ASTM D 86-~~96~~ 03 (~~April 10, 1996~~), ASTM D 850-~~93~~ 03 (~~April 15, 1993~~), ASTM D 1078-~~97~~ 03 (~~July 10, 1997~~), ASTM D 2879-97 (~~April 10, 1997~~), as modified in Appendix B to this Method 310, ASTM D 2887-~~97~~ 02 (~~April 10, 1997~~) and ASTM E 1719-97 (~~March 10, 1997~~).
- 3.6.2 LVP-VOC status of "compounds" or "mixtures." The Executive Officer will test a sample of the LVP-VOC used in the product formulation to determine the boiling point for a compound or for a mixture. If the boiling point exceeds 216° C, the compound or mixture is an LVP-VOC. If the boiling point is less than 216° C, then the weight percent of the mixture which boils above 216° C is an LVP-VOC. The Executive Officer will use the nearest 5 percent distillation cut that is greater than 216° C as determined under 3.6.1 to determine the percentage of the mixture qualifying as an LVP-VOC.
- 3.6.3 Reference method for identification of LVP-VOC compounds and mixtures. If a product does not qualify as an LVP-VOC under 3.6.2, the Executive Officer will test a sample of the compound or mixture used in a products formulation utilizing one or both of the following: ASTM D 2879-97, as modified in Appendix B to this Method 310, and ASTM E 1719-97, to determine if the compound or mixture meets the requirements of Title 17, CCR, section 94508(a)(~~78~~ ***)(A).

3.7 Final Determination of VOC Content

If a product's compliance status is not satisfactorily resolved under sections 3.5 and 3.6, the Executive Officer will conduct further analyses and testing as necessary to verify the formulation data.

- 3.7.1 If the accuracy of the supplied formulation data is verified and the product sample is determined to meet the applicable VOC standards, then no enforcement action for violation of the VOC standards will be taken.
- 3.7.2 If the Executive Officer is unable to verify the accuracy of the supplied formulation data, then the Executive Officer will request the product manufacturer or responsible party to supply information to explain the discrepancy.
- 3.7.3 If there exists a discrepancy that cannot be resolved between the results of Method 310 and the supplied formulation data, then the results of Method 310 shall take precedence over the supplied formulation data. The results of Method 310 shall then determine if the product is in compliance with the applicable VOC standards, and may be used to establish a violation of ARB regulations.

4 CALCULATION OF VOC CONTENT

This section specifies the procedure for calculating and determining the final VOC content of a product, which is reported as ~~a single~~ percent by weight of VOC.

4.1 Aerosol Products

- 4.1.1 For aerosol products, except those containing LVP-VOC, the percent VOC content shall be calculated using the following equation:

$$\% \text{ VOC} = \frac{\text{WL} (\text{TV} - \text{A} - \text{H} - \text{EL}) + \text{WP} - \text{EP}}{\text{WL} + \text{WP}} \times 100$$

Where²:

WL = weight (gm) of ~~liquid product~~ the non-propellant portion, excluding container and packaging

TV = weight fraction of non-propellant total volatile material (US EPA Reference Methods 24/24A, ASTM D 2369-~~97~~ 03)

²Alternate test methods, as provided in section 7.0 6.0, or appropriate approved methods from section 2.0 may be used.

- A = weight fraction of ammonia (as NH₄) in liquid the non-propellant portion (ASTM D 1426-~~93~~ 03) or US EPA Method 300.7
- H = weight fraction of water in liquid the non-propellant portion (ASTM D 3792-~~91~~ 99 or ASTM D 4017-~~96a~~ 02)
- EL = weight fraction of exempt compounds in liquid the non-propellant portion (US EPA Method 8240B, US EPA Method 8260B, US EPA Reference Method 18, ASTM D 859-94, NIOSH Method 1400), ~~ASTM D 86-96, ASTM D 850-93, ASTM D 1078-97, ASTM D 2879-97, as modified in Appendix B to this Method 310, ASTM D 2887-97, ASTM E 1719-97. LVP-VOCs are exempted in accordance with section 94508(a)(78).~~
- WP = weight (gm) of propellant (ASTM D 3074-94 [as modified and include ASTM D 3064-~~89~~ 97] or ASTM D 3063-94 [as modified and include ASTM D 3064-~~89~~ 97]), excluding container and package.
- EP = weight (gm) of exempt compounds in propellant (US EPA Reference Method 18)

4.1.2 For aerosol products containing LVP-VOC, the percent VOC shall be calculated using the following equation:

$$\% \text{ VOC} = \frac{\text{WL}[(1 - H) \times (1 - \text{LVP}) - \text{EL}] + (\text{WP} - \text{EP})}{\text{WL} + \text{WP}} \times 100$$

Where:

LVP = weight fraction of LVP-VOC compounds and/or mixtures in the non-propellant portion (ASTM D 86-03, ASTM D 850-03, ASTM D 1078-03, ASTM D 2879-97, as modified in Appendix B to this Method 310, ASTM D 2887-02, ASTM E 1719-97. LVP-VOCs are exempted in accordance with section 94508(a)(***).

4.2 Non-Aerosol Products

4.2.1 For non-aerosol products, except those containing LVP-VOC, the percent VOC content shall be calculated using the following equation:

$$\% \text{ VOC} = (\text{TV} - \text{A} - \text{H} - \text{EL}) \times 100$$

4.2.2 For non-aerosol products containing LVP-VOC, the percent VOC shall be calculated using the following equation:

$$\% \text{ VOC} = [(1 - H) \times (1 - \text{LVP}) - \text{EL}] \times 100$$

5 TESTING TO DETERMINE REACTIVE ORGANIC COMPOUNDS IN AEROSOL COATING PRODUCTS

This section specifies the procedure for determining the percent by weight of the reactive organic compounds contained in aerosol coating products, for the purpose of determining compliance with the Aerosol Coatings Regulation.

- 5.1 The testing begins when the Executive Officer selects a product for analysis. The Executive Officer will maintain sample chain of custody throughout the selection and analytical process. When a product is selected for testing, the Executive Officer will request the product manufacturer or responsible party to supply the product formulation data specified in Title 17, CCR, section 94526(b)(2). The manufacturer or responsible party shall supply the requested information within 10 working days. Information submitted to the Executive Officer may be claimed as confidential; such information will be handled in accordance with the confidentiality procedures specified in sections 91000 to 91022, Title 17, CCR.

5.2 Initial Testing of the Propellant Portion of Aerosol Coating Products

The aerosol propellant is separated from the non-propellant portion of the product by using ASTM D 3074-94 (as modified in Appendix A for metal aerosol container) or ASTM D 3063-94 (as modified in Appendix A for glass aerosol container). The propellant portion is analyzed for reactive organic compounds and other compounds by using US EPA Reference Method 18. The remaining non-propellant portion of the product is then analyzed as specified in section 5.3.

5.3 Initial Testing of the Non-Propellant Portion of Aerosol Coating Products

The non-propellant portion of the product sample is analyzed to determine the reactive organic compounds in the sample, including the presence of any prohibited compounds. This analysis is conducted by performing the following tests:³

- 5.3.1 Gravimetric analysis of samples to determine the weight percent of total volatile material, using US EPA Reference Methods 24/24A, ASTM D 2369-~~97~~ 03.
- 5.3.2 Determination of sample water content. For determination of water content either ASTM D 4017-~~96a~~ 02, or ASTM D 3792-~~94~~ 99 may be used, or results from both procedures may be averaged and that value reported.
- 5.3.3 Determination of ammonium content using ASTM D 1426-~~93~~ 03 or US EPA Method 300.7.
- 5.3.4 Determination of ketones and alcohol content using NIOSH Method 1400.

³ Alternate test methods may be used, as provided in section 7.0

- 5.3.5 Analysis of reactive organic compounds and, if present, prohibited compounds (US EPA Reference Method 18, US EPA Method 8240B, US EPA Method 8260B, ASTM D 859-94 00, NIOSH Method 1400).

5.4 Prohibited Compounds

If the sample is found to contain compounds prohibited by the Aerosol Coatings Regulation (e.g., ozone-depleting compounds) at concentrations equal to or exceeding 0.1 percent by weight, the Executive Officer will reanalyze the sample for confirmation.

5.5 Initial Determination and Verification of Reactive Organic Compound Content

The Executive Officer will determine the reactive organic compound content by verifying formulation data pursuant to sections 5.2 and 5.3. Only those components with concentrations equal to or greater than 0.1 percent by weight will be reported.

- 5.5.1 Based on manufacturers formulation data and the analysis conducted under section 5, the Executive Officer will make an initial determination of whether the product meets the applicable requirements specified in the Aerosol Coatings Regulation. If initial results show that the product does not meet the applicable requirements, the Executive Officer may perform additional testing to confirm the initial results.

5.6 Final Determination of Reactive Organic Compound Content

If a product's status is not satisfactorily resolved under section 5.1 - 5.5, the Executive Officer may conduct additional analyses and testing as necessary to verify the formulation data.

- 5.6.1 If the Executive Officer is unable to verify the accuracy of the supplied formulation data, then the Executive Officer will request the product manufacturer or responsible party to supply additional information to explain the discrepancy.
- 5.6.2 If the additional information supplied by the manufacturer or responsible party shows that the product does not meet the applicable requirements, then the Executive Officer will take appropriate enforcement action.
- 5.6.3 If the manufacturer or responsible party fails to provide additional information as specified in section 5.6.1, the initial determination of reactive organic compound content under section 5.1 - 5.5 shall determine if the product is in compliance with the applicable reactive organic compound limits. This determination may be used to establish a violation of the Aerosol Coatings Regulation.
- 5.6.4 If there exists a discrepancy that cannot be resolved between the results of Method 310 and the formulation data or additional information supplied by the manufacturer or responsible party, then the results of Method 310 shall take precedence over the supplied formulation data or additional information. The results of Method 310 shall

then determine if the product is in compliance with the applicable requirements, and may be used to establish a violation of the Aerosol Coatings Regulation.

6 METHOD PRECISION AND ACCURACY

- 6.1 The precision of Method 310 for determining VOC content was evaluated using seven representative products with known volatile organic compound (VOC) contents ranging from 6.2 to 81.2 percent VOC by weight. Each sample was divided into six portions, and each portion was separately analyzed to determine the VOC content. Based on the results of this analysis, the 95 percent confidence interval for Method 310 is 3.0 percent by weight (Wt/Wt%).
- 6.2 For determining the percent by weight of the individual ingredients in aerosol coating products, the precision and accuracy of the determination for each ingredient is governed by the precision and accuracy of the test method used to ascertain the percent by weight of each ingredient.

7 ALTERNATE TEST METHODS

Alternative test methods which are shown to accurately determine the concentration of VOCs or constituent components in antiperspirant/deodorants, consumer products, or aerosol coating products (or their emissions) may be used upon written approval of the Executive Officer.